CHAPTER 2

LITERATURE REVIEW AND OBJECTIVES

The detailed literature review on hydrogen-based proton exchange membrane fuel cells for development to provide low cost power has led to the identification of significant research gaps and based on the most significant research gaps after thorough literature review, the objectives are discussed in this chapter. The working principles of proton exchange membrane fuel cells (PEMFC), main components of PEMFC, characterization of cathode electrode electrocatalysts, and the performance of a hydrogen based PEMFC are thereby discussed in this chapter.

2.1 Proton exchange membrane fuel cell advancement

The polymer electrolyte membrane (PEM) fuel cell, often referred to as a proton exchange membrane fuel cell (PEMFC), is a kind of fuel cell that is primarily being developed for transportation purposes, as well as for stationary fuel cell applications and portable fuel cell applications. The proton exchange membrane fuel cell (PEMFC), also known as the solid polymer fuel cell (SPFC), was invented in the 1960 by General Electric for use in first manned space vehicles mission of national aeronautics and space administration, America (Larminie and Dicks 2003). A unique proton conduction polymer electrolyte membrane and lower temperature range (30 to 100 °C) is its distinctive characteristics for the electricity production by PEMFCs. The membrane electrode assembly (MEA) that include electrodes, an electrolyte, an electrocatalyst, and a gas diffusion layer are the foundation of PEMFC construction. The electrolyte is an ion conduction polymer to which an electrocatalytic porous electrode is attached on each side. The anode-electrolyte-cathode assembly is thus a single unit and extremely thin. These membrane electrode assemblies (MEA) are commonly connected in series using a bipolar plate. The mobile ion in the polymers utilized is an H^+ ion or proton, the basic operation of the cell is significant the same as that of an acid electrolyte fuel cell (Choudhary and Pramanik 2020a). The polymer electrolytes work at low temperatures, a PEMFC can start rapidly, because the MEA is thin, so that compact nature of fuel cells can be created (Singh and Pramanik 2022). There are no hazardous fluid dangers, and the cell can operate in any location. As a result, the PEMFC is ideal for usage in automobiles and portable applications (Carrette et al., 2001). Early versions of the PEMFC, like as those used in Gemini spacecraft of NASA, had a small lifespan of some hours, but it was sufficient for those early missions. It was decided not to pursue the commercial development of the PEMFC due to the high cost compared to other fuel cells, such as the phosphoric acid fuel cell that was then being developed, as well as the problem of water management in the electrolyte, which was too challenging to manage reliably. The development program was carried on with the inclusion of a new polymer membrane like, nafion was a registered brand of Dupont in 1967. These membranes are much more stable than polystyrene sulfonate membranes and have higher conductivity and acidity. A polytetrafluoroethylene (PTFE) based structure makes up the Nafion, which is chemically inert in both reducing and oxidizing conditions. The equivalent weight, which is inversely correlated to the ion-exchange capacity and is defined as the weight of polymer that will neutralize one equivalent of base, is the distinguishing property of proton conducting polymer membranes. The advancements made in recent years have increased density significantly while simultaneously reducing the consumption of platinum (Maiti et al., 2022). These advancements have resulted in a significant decrease in cost per kilowatt of power and enormous rise in power density. The PEMFCs are actively being developed for use in automobiles and public transportation vehicles, as well as for a huge variety of portable applications (Chen and

Laghrouche 2021; Lou et al., 2021). It might be argued that PEMFCs have more potential uses than any other electrical energy generation technology. In view of this, for the last two decades, researchers across the world are involved in the research and development actively for the manufacturing of low cost fuel cell components like anode electrocatalyst (Ke et al., 2022), cathode electrocatalyst (Polagani et al., 2024), proton exchange membrane (Jiang et al., 2021), and GDL (Athanasaki et al., 2023). In the present thesis, development of cathode electrocatalyst using non noble metal with Platinum (Pt) is considered to enhance the oxygen reduction reaction kinetics of cathode.

2.1.1 Main components of proton exchange membrane fuel cell (PEMFC)

The anode and cathode electrodes, electrolyte, fuel, and oxidant compose the components of the proton exchange membrane fuel cell. The electrocatalyst is the main functioning part of the anode and cathode electrode. The polymeric solid proton exchange membrane is used as electrolyte keeping in between anode and cathode electrode, and further hot pressed/clamped to use the assembly as MEA in PEMFC. Fuel and oxidant are supplied through anode and cathode side. The next subsections, various components like electrolyte, anode and cathode electrocatalyst materials, electrooxidation of hydrogen and oxygen reduction reactions are discussed.

2.1.1.1 Membrane electrolyte

Although Nafion® is the widely studied and used electrolyte for PEM based fuel cells, additional perfluorocarbon sulfonic acid membranes from Dow, Gore, and Asahi Chemical are also used and studied (Singh and Pramanik 2022; Wakizoe et al., 1995; Yeager and Steck 1981). Membranes typically have a narrow temperature range typically (30 ºC to 100 ºC) over which they are stable. The maximum temperature limit is determined by the retention rate of water by the membrane humidification, as water is exhibited for H^+ ion conduction through membrane electrolyte. However, the manufacturing of composite membrane improves membrane structure and conductivity. This can be accomplished in a variety of methods, one of which is to reinforce the perfluorosulfonic membrane with PTFE components, as Gore and Asahi Chemicals have done successfully (Wakizoe et al., 1995 and Liu et al., 2024). Another option is to saturate a membrane with a solution or a solid in order to reduce the permeability of the reactant gases (Peighambardoust et al., 2024). Another method is to dissolve the membrane in a suitable solvent and mix it with another substance (Figoli et al., 2014). The composite membrane can be employed in a fuel cell, after it has been recast (Broka and Ekdunge 1997 and Pu et al., 2014). To develop thinner membranes and reduce membrane resistance in the system, PTFE sheets were also impregnated with Nafion ionomer (18 wt. % Nafion® in EtOH) (Nouel and Fedkiw 1998). This membrane has a conductivity comparable to Nafion® 112 (0.1 Scm-1) but a higher permeability to gases. The Polyvinylidene fluoride (PVDF) sheets grafted with radiation produced membranes with lower oxygen solubility but higher diffusion than Nafion membranes (Sadeghi et al., 2018). As long as these membranes are physically and electrochemically stable, they hold potential for PEM fuel cells. Recently, Goo et al., 2020, Zhang et al., 2019 and Ye et al., 2011 develop proton exchange membrane for hydrogen-based fuel cell application. The membrane electrolyte developed by Goo et al., 2020 using sulfonated hydrocarbon-based polymer to synthesized nafion composite membranes through coating and blending. The membrane was characterized by electrochemical impedance spectroscopy (EIS) to determine ionic conductivity. The conductivity was found in the range of 223.3 $mScm^{-1}$ (80 °C). However, the membrane has anisotropic swelling and dimensional instability problem. Similarly, Ye et al., 2011 synthesized nafion-titania nanocomposite membranes using an in situ sol-gel method by hydrolyzing and condensing precursors using nafion solution. The proton conductivity of this electrolyte membrane is of the order 5x10^{-3} Scm^{-1} (100 °C). In Present study Nafion® 117 is used as electrolyte membrane for proton exchange membrane fuel cell due to its excellent mechanical, thermal, and chemical activity. Apart from this the ionic conductivity of Nafion® 117 is also very high (Choudhary and Pramanik 2019).

2.1.1.2 Electrodes

To ensure that reactant gases are supplied to the active zones where the noble metal electrocatalyst is in good contact with the ionic and electronic conductor, PEM fuel cell electrodes are made typically porous for gas diffusion. It takes careful preparation and attention to create gas diffusion assembly (GDA), and each step of the process is crucial. It is well known that an electrode must have a three-phase boundary (Choudhary and Pramanik 2019) between the reactants (fuel/oxidant) supply, the electrocatalyst particle, and the ionic conductor on one side i.e., membrane electrolyte. To ensure that electrons are delivered to or removed from the reaction site, the particles must come into direct contact with an electronic conductor (Figure 2.1). The electrocatalyst particles are often supported on a carbon substrate, which typically provides electronic conductivity.

The anode and cathode electrode are generally prepared from the electrocatalyst, activated carbon and mixture of Nafion® ionomer and PTFE dispersion, which acted as binders. The PTFE, along with pores, provide a flow network which allows easy escape of the reaction products from electrode surface. Typically, GDL for electrode preparation uses Toray carbon paper or carbon cloths. The electrocatalyst layer is covered with an ionomeric binder i.e., Nafion® solution before the electrode is pressed or clumped against the membrane to create the three-phase assembly. Thus, the majority of electrocatalyst particles will have good ionic interaction with the ionomer material covering the membrane. When utilizing humidified gases the electrocatalyst layer must be hydrophobic enough to keep the pores from flooding. This hydrophobicity can be achieved by combining hydrophobic PTFE as a binder with hydrophilic Nafion®. The choice of electrocatalyst based on fuel, oxidant, and electrolyte medium, affects the performance of PEMFC. The most active and efficient part of an electrode is the electrocatalyst, which actively participate in the electrooxidation at the anode and reduction processes at the cathode of the cell. There are various types of electrocatalysts that have been used so far for anode and cathode fabrication of a hydrogen based PEMFC. (Ramli et al., 2024; Etesami et al., 2022 and Zhang et al., 2021). The anode and cathode electrocatalyst are discussed in the subsequent section.

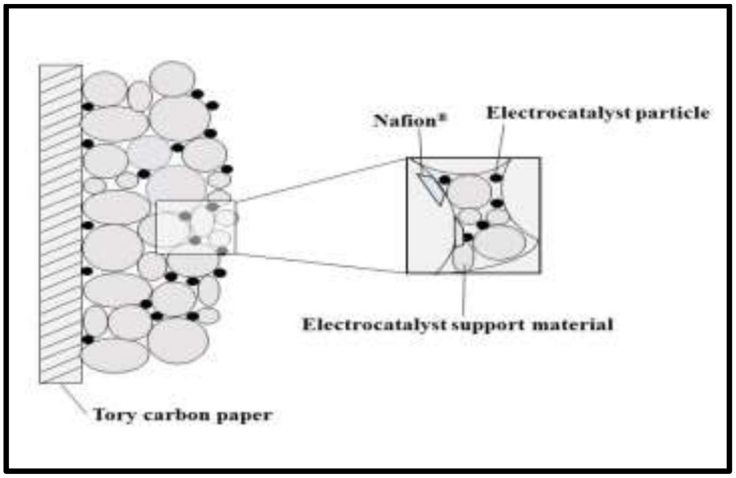


Figure 2.1 Three phase network formed by electrocatalyst particles, inomer and gas phase in a porous structure, ensuring both electronic and ionic contact as well as gas transport.

2.1.1.3 Anode electrocatalyst material

The anode performs well when pure hydrogen is utilized as fuel with pure Pt catalyzing the electrooxidation of hydrogen (Fan et al., 2022; Seo et al., 2020; Tzorbatzoglou et al., 2018 and Durst et al., 2014). However, in most fuel cells, which use other fuel stream like, ethanol methanol, glycerol etc, the electrooxidation become very difficult on pure Pt electrocatalyst due to the complex molecular structure of these alcohols (Ke et al., 2022; Choudhary and Pramanik 2020b; Gupta and Pramanik 2019 and Ball et al., 2007). All of these above substances have the potential to deactivate the anode electrocatalysts to varying degrees due to formation of some complex.

The low-temperature fuel cells based on hydrogen fuel also suffers from CO poisoning of the Pt electrocatalyst if hydrogen fuel contains CO or impurities (Dubau et al., 2014 and Oetjen et al., 1996). The CO poisoning occurs in PEMFC due to the adsorption of the CO species to the active sites of the platinum electrocatalysts, resulting in no, or almost no, sites available for reaction with H_2 (Molochas and Tsiakaras 2021). The performance of the anode reaction is determined by (i) the interaction between the electrocatalyst surface and the fuel hydrogen, (ii) formation of absorbed species and interaction with the electrocatalyst surface (Equation 2.1), and (iii) formation of H^+ ions and electrons (Equation 2.2). Since the kinetics of electrooxidation on Pt electrocatalyst is extremely fast. As already mentioned on Pt-based electrocatalysts, the electrooxidation of hydrogen occurs easily. In a PEMFC, the oxidation of hydrogen at higher current densities is usually restricted by mass-transfer from bulk phase to active electrocatalyst sites. Further, the adsorption of the hydrogen gas onto the electrocatalyst surface, followed by the dissociation of hydrogen and an electrochemical reaction that produces two hydrogen ions, are important reaction steps in the oxidation of hydrogen occurs as following (Equation 2.1 to 2.3) (Lei et al., 2019; Wang et al., 2009 and Carrette et al., 2001).

$$2\mathrm{Pt}_{(s)} + \mathrm{H}_2 \rightarrow \mathrm{Pt} - \mathrm{H}_{\mathrm{ads}} + \mathrm{Pt} - \mathrm{H}_{\mathrm{ads}} \tag{2.1}$$

$$2(\mathrm{Pt} - \mathrm{H}_{\mathrm{ads}}) \rightarrow 2\mathrm{H}^+ + 2\mathrm{e}^- + 2\mathrm{Pt}_{(s)} \tag{2.2}$$

Where Pt-H_{ads} is an adsorbed H-atom on the Pt active site and $Pt_{(s)}$ is a free surface site.

The overall result of hydrogen oxidation is:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{2.3}$$

It is well known that in proton exchange membrane fuel (PEMFC), Pt/C is the most often used as anode active electrocatalyst material (sun et al., 2022; Singh and Pramanik 2022; Shroti and Daletou 2022; Ohyagi and Sasaki 2013; Termpornvithit et al., 2012 and Iyuke et al., 2003). The noble metal Pt is very expensive also is not available easily (Singh and Pramanik 2024). Many researchers have been focusing on developing Pt-alloyed Pt-X (where X = Mo, W etc) electrocatalysts to reduce the excessive use of expensive Pt electrocatalyst (Ke et al., 2022 and Serov and Kwak 2009). Molochas and Tsiakaras (2021) found that when Pt alloyed with Mo and W, the sufficient incorporation of Mo and W with Pt ensure adequate stability of PEMFC for longer duration as well as enhance the CO tolerance through bifunctional characteristics of Mo and W. Although, some bimetallic electrocatalyst have been developed for electrooxidation of hydrogen, the performance of PEMFC in terms of power density is not promising. Thus, in the current research work, commercial Pt/C (40 wt. %) was chosen as the anode electrocatalyst. To get higher PEMFC performance, the cathode electrocatalyst must be selected as carefully that of anode electrocatalyst. The cathode electrocatalyst is discussed in the next section.

2.1.1.4 Cathode electrocatalyst material

There are many cathode electrocatalyst for oxygen reduction reaction (ORR) available such as pure Pd, Pt, Rh, Ir metal and its metal-alloy etc (Ramli et al., 2024 and Antolini 2014). The electrocatalytic activity of Pt towards ORR strongly depends on its O_2 adsorption energy, the dissociation energy of the O-O bond, and the binding energy of OH on the Pt surface. The electronic structure of the Pt catalyst (Pt *d*-band vacancy) and the Pt-Pt inter-atomic distance (geometric effect) can strongly affect these energies (Stassi et al., 2006). Theoretical calculations on O_2 and OH binding energy for several metals had predicted that Pt should have the highest electrocatalytic activity among other metals with the ORR activity of Pt > Pd > Ir > Rh (Norskov et al., 2004). The activity of electrocatalyst enhancement occurs when Pt is alloyed with other metals that can be explained by the change in electronic structure i.e., the increased Pt *d*-band vacancy and in geometric effect i.e., Pt-Pt inter-atomic distance). Alloying of other metals like Co, Ni, Cu etc with Pt causes a lattice contraction, leading to a more favorable Pt-Pt distance for the dissociative adsorption of O_2 (Singh and Pramanik 2022; Antolini et al., 2005). Till date, Pt catalysts have the broad applications in fuel cells for their high catalytic activity and long durability (Singh and Pramanik 2022; Zhang et al., 2020; Lai et al., 2015a; Wang et al., 2014; Demazeau et al., 2010 and Iyuke et al., 2003). However, using pure Pt as electrocatalyst supported on high surface area carbon powder as support material is very costly and not economical. So instead of pure Pt/C electrocatalyst, the idea of Pt-based bimetallic alloys has been used widely for the oxygen reduction reaction studies, due to their high activity and excellent stability in acidic medium. It is possible to alloy Pt with transition metal (M) (where, M = Co, Ni, Cu and Pd) to minimize the content of Pt as well as cost of electrocatalyst and improve the electrocatalytic performance. The synthesized electrocatalyst could reduce the surface adsorption of the products and/or intermediated species, causing the increase in the active sites accessible for fresh reactants (Zhang et al., 2021; Kulkarni et al., 2018; Wang et al., 2015b; Zheng et al., 2014; Jayasayee et al., 2012 and Jang et al., 2011). The laboratory based synthesized Pt-based bimetallic alloys provides abundant active sites, ordered structures and Pt-rich surfaces as compared to commercial costly Pt/C electrocatalyst (Zhang et al., 2019; Wang et al., 2018b; Xia et al., 2015 and Zhang et al., 2003). Recently, several studies on the oxygen reduction reaction, using Pt-based bimetallic electrocatalysts like Pt-Co (Sun et al., 2022; Singh and Pramanik 2022; Sneed et al., 2018; Deshpande et al., 2016; Yang et al., 2016 and Guo et al., 2013), Pt-Ni (Tian et al., 2019; Gong et al., 2019; Lin et al., 2018; Shen et al., 2015a; Zhang et al., 2010; Lia et al., 2015 and Stamenkovic et al., 2007) and Pt-Fe (Wang et al., 2018a; Wang et al., 2015 and Shui et al., 2001), Pt-Cu (Zhou and Zhang 2015; Liu et al., 2014), Pt-Pd (Liu et al., 2012; Lee et al., 2012 and Zhang et al., 2012) have been studied. Apart from bimetallic electrocatalyst, trimetallic electrocatalyst via Pt-Co-Fe (Yang et al., 2023), Pt-Ni-Cu (Liu et al., 2014), Pt-Cu-Ag (Zhou and Zhang 2015), Pt-Pd-Cu (An et al., 2018), and Pt-Pd-Au (Lankiang et al., 2015) have also been tested. The performance reported by the trimetallic electrocatalyst for ORR is not promising to that of bimetallic electrocatalyst. It should be noted, that there are rarely commercially available Pt-based bimetallic electrocatalysts for oxygen reduction reaction. On the other side, the laboratory synthesized majority of the bimetallic electrocatalysts used for ORR. Yet need to be improved to achieve the performance similar to the commercial single metal Pt electrocatalyst with high Pt metal content. In view of this Pt-based bimetallic cathode electrocatalyst for ORR is very much efficient. The present thesis focuses on the synthesis of the Pt-based electrocatalyst for subsequent use in the H_2 based proton exchange membrane fuel cell. It should be noted that the synthesis method and solvent used is the process both play an important role. Till date, no detailed research on the synthesis of cathode electrocatalysts utilizing various types of solvents, as well as thorough characterization of the synthesized electrocatalyst had not been reported. In this regard, bimetallic Pt-Co and Pt-Ni electrocatalysts for effective ORR in hydrogen-based PEMFCs were synthesized in the laboratory utilizing various solvents. The composition of the metal were varied to manufacture four different types of bimetallic cathode electrocatalyst. Four different types of solvents were used namely, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and ethylene glycol (EG) and Water

(W). The electrocatalyst preparation method for cathode electrocatalyst is discussed in the next section.

2.1.1.4.1 Cathode electrocatalyst preparation methods

The electrocatalyst employed for oxygen reduction reaction in half-cell and in single PEMFC can be synthesized using various method. A number of approaches have been reported in the literature. The electrocatalysts with varied electrochemical activity, surface area, particle size, crystallite size, mean particle size and shape are produced by the various synthesis methods. All of these properties control electrochemical activity of the synthesized electrocatalysts. The often employed important methods for the laboratory synthesizing electrocatalyst include bulk preparation method, which includes chemical vapor deposition method (Dursun et al., 2020 and Esmaeilifar et al., 2010), precipitation method (Yang et al 2012), sol-gel method (Omeiza et al., 2023), solvothermal method (Lin et al., 2018) and hydrothermal method (Mirzaei et al., 2017), impregnation method (Jung et al., 2017) and physical mixing method (Liu et al., 2022). The solvothermal method is the most widely used in recent time among the above mentioned methods due to it has many benefits, including being easy control, affordable, simple process, and high yield of desired electrocatalysts (Lai et al., 2015b; Carpenter et al., 2012 and Demazeau 2010). The synthesized electrocatalysts are sometimes reduced using the hydrogen reduction method (Choudhary and Pramanik 2020b; Panjiara and Pramanik 2020) to improve electrocatalytic property of electrocatalyst. Thus, in the present work solvothermal method was selected for synthesis of Pt-based bimetallic cathode electrocatalyst. Cui et al., (2012) found that octahedral Pt-Ni alloy nanoparticles synthesized from co-reduction of Ni(acac)$_2$ and Pt(acac)$_2$ in presence of dimethylformamide (DMF) at higher temperature 200 °C, where DMF acts as like complexing agent, solvent, and reducing agent. In this study, high heating rates (10 °C/min) and a lower reaction temperature of (120) °C were maintained. A high heating rate resulted in a short induction time and high nucleation rates generating a large number of small electrocatalysts. The choice of precursor ligands controls the shape, while the reaction time tunes the surface of Pt:Ni composition. The synthesized electrocatalyst of 9.5 nm sized Pt-Ni octahedra reached a 10-fold surface area-specific as well as an unprecedented 10-fold Pt mass based activity gain over the state-of-art Pt electrocatalyst, approaching the theoretically predicted limits. Lia et al., (2015) synthesized Pt-Ni octahedral, truncated octahedral, and cubic nanocrystals which were prepared by solvothermal treatment of a mixture of benzyl alcohol containing Pt(acac)$_2$, Ni(acac)$_2$ and polyvinylpyrrolidone (PVP) in the presence of the growth inhibition agent benzoic acid, aniline, as well as potassium bromide and carbon monoxide at the temperature of 150 ^{o}C. The benzoic alcohol was used as solvent and reducing agent both. The selective adsorption of carbon monoxide and bromide on to (100) crystal faces induces the formation of nanocubes. Xu et al., (2014) synthesized Pt-Ni concave nanocrystal by heating mixture of H_2PtCl_6, $NiCl_2$, polyvinyalpyrrolodone, and glycine as solvent using one-pot wet chemical reduction method. The morphological change from concave nanocubes, to nanocubes, and hexoctahedra occurs as glycine concentrations increased. Glycine plays a vital role in tuning the nucleation growth rate of Pt-Ni alloys nanoparticles. Jiang et al., (2017) developed Pt-Co nanoparticle using a one-pot solvothermal method for the synthesis of $Pt_{76}Co_{24}$ nanomyriapods with abundant active sites. The $Pt_{76}Co_{24}$ was synthesized using adequate amount of cetyltrimethylammonium chloride (CTAC) mixed in oleylamine along with Co, Pt precursors and L-glutamine acid. Here, L-glutamic acid and CTAC were used as the green reductant and structure director, respectively. The homogeneous reaction mixture kept in Teflon lined stainless steel autoclave for continuous heating for 12 h at the temperature of 180 ^{o}C. Finally, deposited $Pt_{76}Co_{24}$ nanoparticles on electrocatalyst support was found. Jang et al., (2011) achieved 2-3 nm sized Pt_3Co nanoparticles (NPs) with Pt-enriched shells on a carbon support. The electrocatalysts were prepared by a one-step ultrasound polyol process on carbon support material. In this method a high-intensity ultrasonic probe (Sonic and Materials, model VC-500, amplitude 30%, 13 mm solid probe, 20 kHz) was used to produce ultrasound waves into a solution of $Pt(acac)_2$ and $Co(acac)_2$ (Aldrich) in ethylene glycol (EG) with a porous carbon support (Ketjen Black) added at 150 ºC for 3 h under inert environment of argon gas. The solid final product Pt_3Co nanoparticles was filtered, washed with ethanol, and dried under vacuum. Carpenter et al., (2012) synthesized Pt alloy nanoparticles by solvothermal processes using dimethylformamide (DMF) in a sealed, PTFE lined container. In typical synthesis Pt acetylacetonates and Ni acetylacetonates were dissolved in 12 mL DMF. The reaction mixture was heated at 200 ºC in PTFE-lined glass vials through heating furnace for 24 hr. The PTFE container then removed from the furnace and allowed to cool to ambient temperature before opening. The produced alloy precipitate mixture was sonicated within an ultrasonic water bath for 30 min and was then added to 25 mL of ethanol in which 150 mg of carbon had already been dispersed for 30 min using ultrasonic water bath at 30 ºC. The combined mixture was sonicated for another 30 min and then stirred for several hours. The solids were separated from the mixture by centrifugation, and the clear light yellow supernatant liquid was removed. The remaining traces of supernatant liquid and unwanted reaction products were removed from the solids with three wash cycle, one with 25 mL acetone and two with 25 mL ethanol. The solids were removed from the final wash by filtration rather than centrifugation and were rinsed briefly with acetone and rinsed several times with distilled water. The prepared electrocatalyst was vacuum dried and followed by collection of finished electrocatalyst. Well-faceted nanoparticles (NPs) of Pt_3Ni were successfully synthesized without capping agents and were found to have ORR specific activities 3-5 times greater than that of a Pt standard electrocatalyst. It is seen from thorough literature survey, that the solvothermal process produced the electrocatalyst with better electrocatalytic activity than other processes. Moreover, solvothermal method is cheap, easy to control which makes it more suitable for the synthesis of ORR electrocatalyst (Demazeau, 2010). Thus, in the present study, the solvothermal method was used for the cathode electrocatalyst synthesis. In the next section, various characterization techniques for physical and electrochemical characterization of synthesized cathode electrocatalysts are discussed.

2.1.1.5 Physical Characterizations of synthesized cathode electrocatalyst

2.1.1.5.1 X-ray diffraction (XRD) characterization

The XRD characterization is essential to determine the physical and structural information of synthesized cathode electrocatalyst. The XRD analysis determine the d-spacing, lattice parameter, and crystallite size of the electrocatalyst using X-rays generated in XRD characterization setup. The synthesized cathode electrocatalyst should be crystalline in nature i.e., analyzed by the XRD characterization. In general the XRD pattern is observed for the 2-theta ranges from 10^o to 90^o which include both amorphous phase as well as crystalline phase. For the amorphous electrocatalyst support material like acetylene black ($C_{AB)}$ the carbon (C) diffraction peak for plane (002) is found in 2-theta range of 25^o to 26^o (Huang et al., 2015). In many open literature it was found that the crystalline planes at about 39^o, 46^o, 67^o, 81^o, and 85^o, which reflect crystalline FCC, were assigned to the crystalline planes of Pt (111), (200), (220), (311), and (222), respectively (Choudhary and Pramanik 2020a; Cuevas-Muniz et al., 2015). The mean crystallite sizes (d_c) calculated by Scherrer's formula (Equation (2.4)) for synthesized electrocatalysts (Safo and Oezaslan 2017). The d-spacing was calculated using Bragg's equation (Equation (2.5)) corresponding to Pt (220) plane for the electrocatalyst synthesized (Safo and Oezaslan 2017; Zahari and Aziz 2012)

$$d_c = \frac{0.9\lambda}{\beta \cos\theta} \tag{2.4}$$

$$n\lambda = 2d_{nkl}\sin\theta \tag{2.5}$$

Where, d_c is calculated crystallite size, λ is X-ray wavelength (0.154 nm), β is the width of the peak (in radius) and θ is the angle at peak position, n is the order of diffraction, d_{hkl} is the interplanar distance between two planes of miller index hkl (Antolini et al., 2005; Lima et al., 2006). Salgado et al., (2004) and Santiago et al., (2007) reported that when the percentage of transition metal in the alloy increases, both lattice spacing and crystallite size decrease, in agreement with lower particle size, which resulting in significant performance improvement in PEMFC. Hyun et al., (2013) selected the Pt plane (220) position to observe the peak shifting in order to determine the alloy formation in the Pt-based bimetallic electrocatalyst Pt-M/C (where M= Ni, Co, and Cu) and they also observed that the doping of transition metal in Pt metal increase the alloying percentage in Pt-M/C electrocatalyst, as shown in Figure 2.2. It is seen from Figure 2.2 that compared to Pt/C, all of the peaks had a larger shift angle. The contraction between the Pt-M alloys indicates that Pt atoms are replaced by the tiny transition metal M during the formation of Pt-M alloy, reducing the interatomic distance between Pt atoms. The Vegard's law was employed to analyze the alloying degrees of the Pt-M/C using structural property determined by XRD (Zhuang et al., 2007). Zhang et al., (2003) analyzed the lattice parameters of detected crystalline metal-alloys from the Bragg's Law using diffraction peak angle and Safo et al., (2017) measured the crystallite size using Scherrer's equation. Thus, in the present study, XRD characterization of the synthesized electrocatalyst is considered.

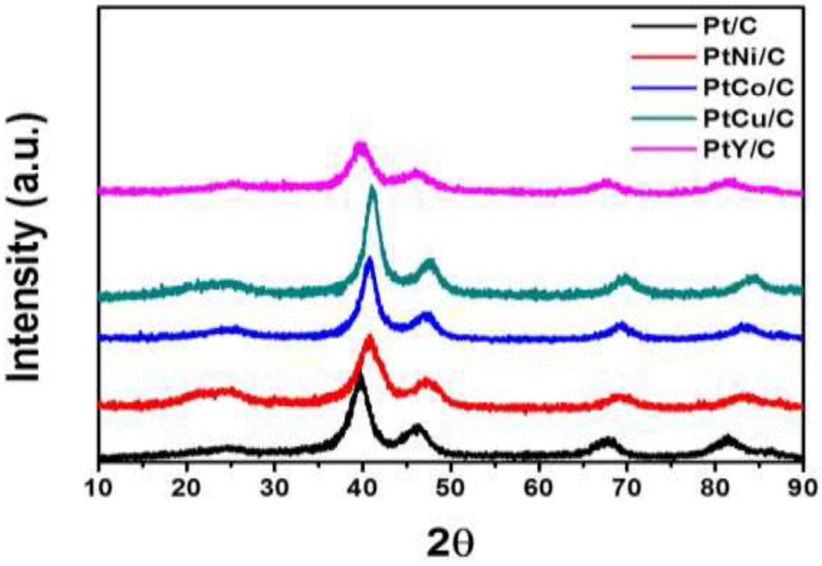


Figure 2.2 The XRD patterns for Pt/C and Pt-M (M = Ni, Co, Cu and Y) electrocatalysts (Hyun et al., 2013).

2.1.1.5.2 Scanning electron microscope (SEM) characterization

The scanning electron microscopy (SEM) is used to examine the surface morphology of the cathode electrocatalyst. The surface properties such as shape, uniformity and surface morphology are determined by SEM investigation. However, it fails to measure the size of the metal particles that are dispersed on electrocatalyst support material. Vinayan et al., (2012) reported, SEM images of Pt_3-Co/C electrocatalyst which shows a homogeneous distribution of metal nanoparticles (Pt_3-Co/C) with an excellent dispersion over the surface of support material when electrocatalyst synthesized at specific condition. Shahgaldi et al., (2015) found that as the electrocatalyst synthesizing condition like temperature, pressure, solvent concentration, and metal loading varies, the morphology of the electrocatalyst changes. The SEM images also provide the information about the agglomeration and phase of metal nanoparticles in the electrocatalyst (Choudhary and Pramanik 2020b).

2.1.1.5.3 Energy dispersive X-ray (EDX) analysis

The presence of metal element is identified using EDX analysis from the elemental mapping of electrocatalyst (Choudhary and Pramanik 2019; Tayal et al., 2012). Another way to detect the presence of metal nanoparticles is color mapping of the elements in the electrocatalysts were also performed by Barim et al., (2020) using EDX. Litkohi et al., (2017) performed EDX analysis to verify the distribution of electrocatalyst particles. However, the particle distribution was not clearly visible in the FESEM images and thus, color mapping analysis was done on electrocatalyst samples. The electrocatalyst particles are clearly distributed uniformly throughout, as it is seen by the color map analysis in Figure 2.3.

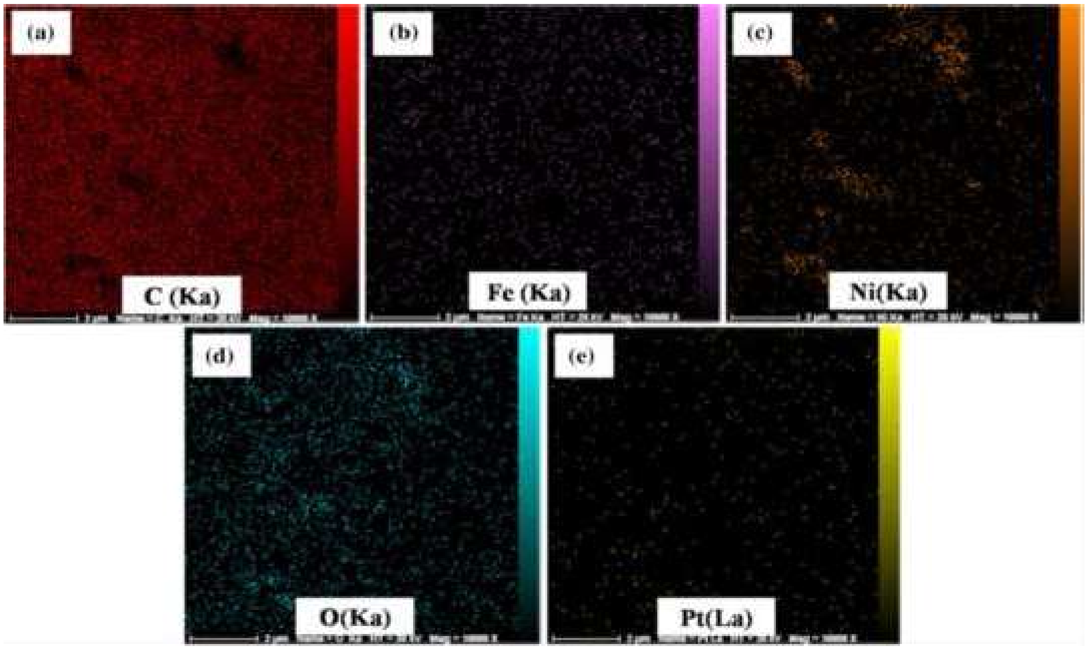
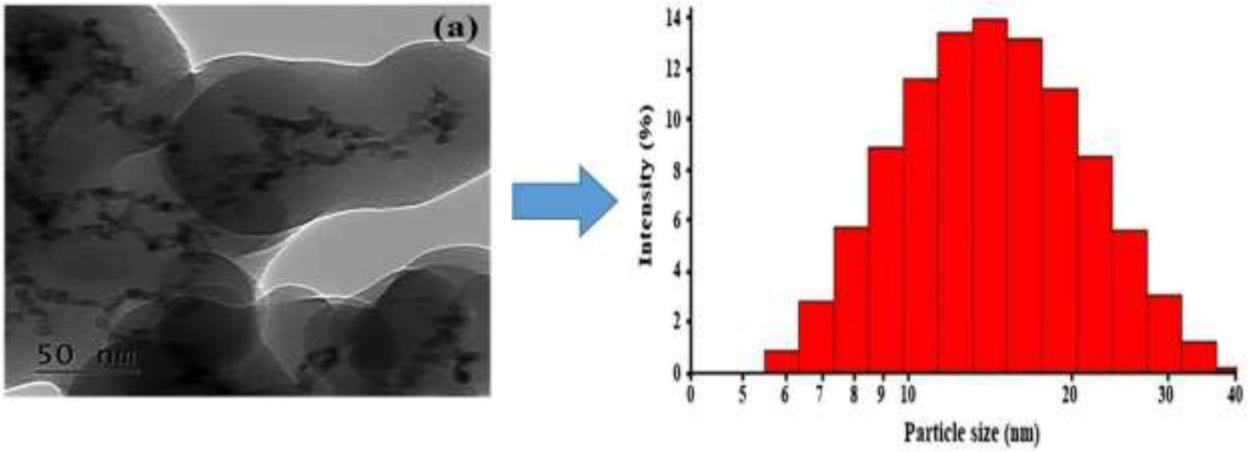


Figure 2.3 Elemental mapping of Pt-Ni-Fe/ICNT/CP, (a) C mapping (b) Fe mapping (c) Ni mapping (d) O mapping (e) Pt mapping (Litkohi et al., 2017).

2.1.1.5.4 Transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) gives the distribution of electrocatalyst particle size and the images of electrocatalyst upto the atomic level (Gummalla et al., 2015). The white particles represent the carbon support material, while dark particles are representing metal nanoparticles (Castagna et al., 2019). Panjiara and Pramanik (2021) estimated the diameter of more than 100 metal nanoparticles in a randomly selected region of the corresponding TEM images for obtaining the average particle size and histograms of the size distribution of the metal nanoparticles. The TEM analysis also shows the exact shape of the metal nanoparticles. Polagani et al., (2023) reported the TEM analysis images and histograms diagram of Pt-Ni/C electrocatalyst of various composition. The TEM images in Figure 2.4 shows that the spherical-shaped Pt and Ni metal nanoparticles are evenly distributed on the carbon support. The range of the particle size is 4-6 nm.



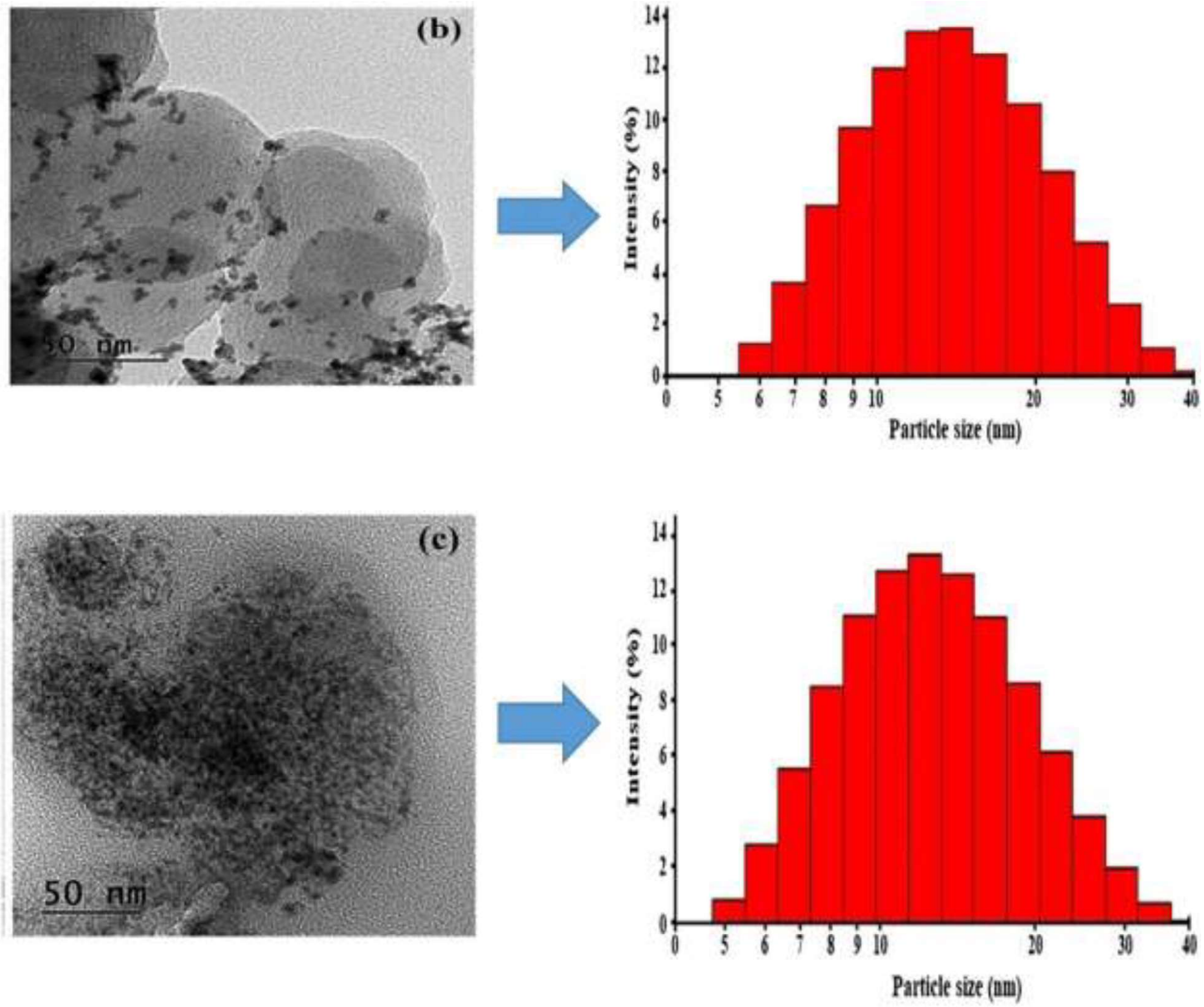


Figure 2.4 TEM images and corresponding particle size distribution profile of varied Pt and Ni compositions on carbon support (a) PNC-1, (b) PNC-2 and (c) PNC-3 (Polagani et al., 2023).

2.1.1.6 Electrochemical characterization of synthesized cathode electrocatalyst

2.1.1.6.1 Cyclic voltammetry (CV) analysis

An effective electrochemical technique for examining the behavior of redox processes in solution is cyclic voltammetry (Esfandiari et al., 2016). The CV test of cathode electrocatalyst is generally performed to obtain important information about reduction kinetics of electrochemical process occurs at cathode in presence of oxidant (Zhang et al, 2005 and Vinayan et al., 2012). The CV is performed in a half-cell using three electrodes assembly namely (i) working electrode where the electrochemical reaction occurs, (ii) counter electrode which complete the circuit and (iii) reference electrode with a standard electrode potential at ambient pressure (Choudhary and Pramanik 2020a). The anodic and cathodic limits are the two extreme potentials between which the potential of working electrode is swept at a controlled rate (Rathoure and Pramanik 2016). The peak positions of CV and shapes provide details on the redox characteristics of the species in solution, including the redox potential i.e., oxidation or reduction potential and the electron transfer kinetics in the reaction (Zhang et al., 2013).

The electrochemical reaction mechanism of oxygen reduction reaction (ORR) is quite complicated and involves many intermediates, primarily depending on the nature of the electrode material, electrocatalyst and electrolyte (Yeager 1986). The oxygen reduction reaction on the Pt electrocatalyst in acidic medium is generally proceeds either two step 2 + 2 electron pathway mechanism Equation (2.7) and Equation (2.9) or single step 4 electron Equation (2.10) The possible reaction mechanism of oxygen reduction at the cathode of a PEMFC is as follows (Xiong et al., 2018 and Arico et al., 2001):

$$\mathrm{O_2 + Pt \rightarrow Pt - O_2} \tag{2.6}$$

$$\mathrm{Pt - O_2 + H^+ + e^- \rightarrow Pt - HO_2} \tag{2.7}$$

$$\mathrm{Pt - HO_2 + Pt \rightarrow Pt - OH + Pt - O} \tag{2.8}$$

$$\mathrm{Pt - OH + Pt - O + 3H^+ + 3e^- \rightarrow 2Pt + 2H_2O} \tag{2.9}$$

Or

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \tag{2.10}$$

Thus, in the cathode compartment, water is the only byproduct, produced by the reduction reaction. The first step of oxygen reduction reaction mechanism on a platinum electrode involves the chemisorption of oxygen molecules on the Pt surface (Equation 2.6 and Equation 2.8) and subsequently oxygen reduction following the steps Equation (2.7) and Equation (2.9) (Pramanik and Basu 2012). Abkar et al., (2022) synthesized Pt-Co(3:1 by wt., 40 wt. %)/NC cathode electrocatalyst and studied the performance of synthesized Pt-Co/NC cathode electrocatalyst using homemade catalyst coated membrane electrode (CCME) in a half-cell tree electrode assembly. The Pt-Co/NC exhibited −58.7 mA/cm^2 at 0.3 V/RHE in half-cell study. They did not study single cell PEMFC which is essential for estimation of actual performance of Pt-Co/NC in single cell in terms of cell voltage and power density. In a half-cell three electrode assembly, Litkohi et al., (2020) investigated the performance of a manufactured Pt-Ni/CNT cathode electrocatalyst utilizing a handmade catalyst-coated membrane electrode (CCME). The half-cell investigation of the Pt-Ni/CNT exhibited the maximum current density of 62.71 mA/cm^2. In order to determine the actual performance of synthesized Pt-Ni/CNT, single cell study was not performed. Pramanik and Basu (2011) reported the CV analysis for the different types of cathode electrocatalyst i.e., Pt-Ru/C, Pt-black HSA, and Pt/C in the oxygen saturated 0.5 M $HClO_4$ at the temperature of 42 ^{o}C. Pt-black HSA cathode exhibit lower activation over potential as compare to Pt/C and Pt-Ru/C. The oxygen reduction peak position for Pt-black HSA, Pt/C and Pt-black HSA were found at potential of 0.526 V, 0.47 V and 0.02 V, respectively as shown in Figure 2.5.

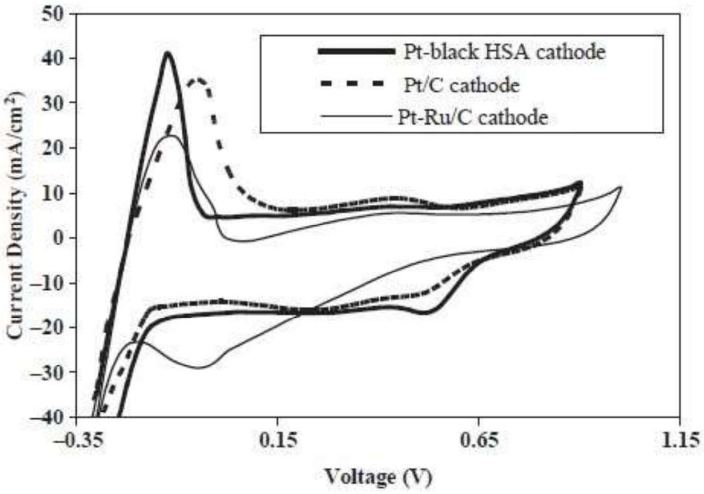
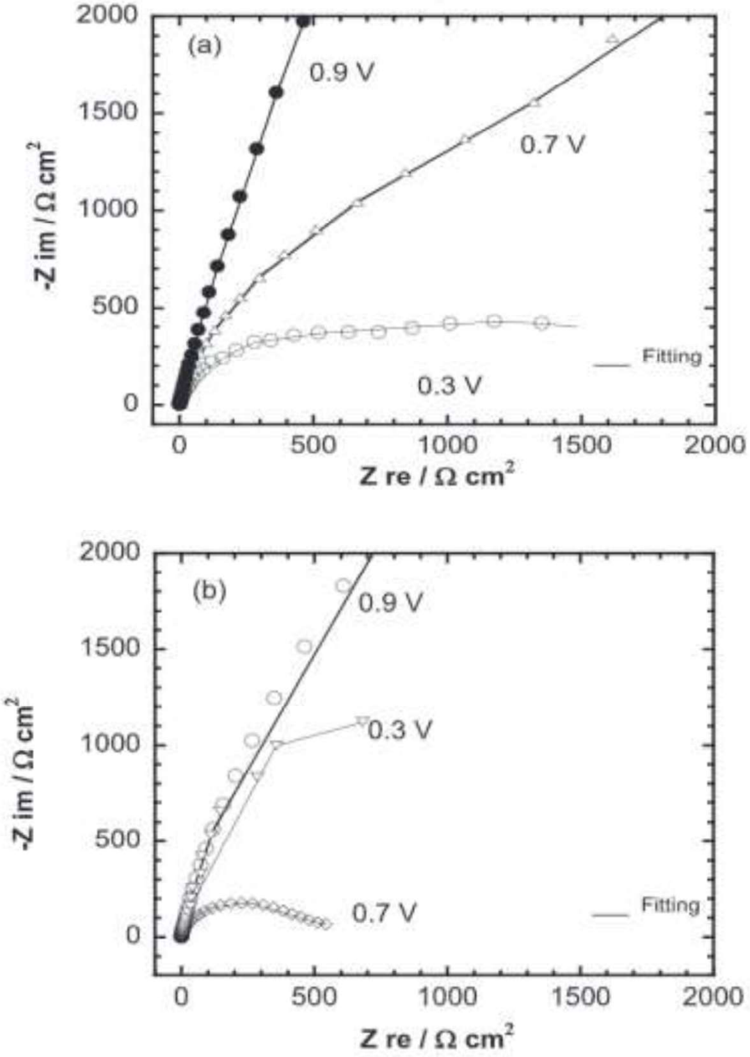


Figure 2.5 Cyclic voltammetry for Pt-Ru/C, Pt-black HSA and Pt/C cathode in the presence of oxygen in 0.5 M HClO4 solution with scan rate of 10 mV/s at 42 ºC (Pramanik and Basu 2011).

2.1.1.6.2 Electrochemical impedance spectroscopy (EIS) analysis

In order to investigate the solution resistance, charge transfer resistance and constant phase element of species in solution, electrochemical impedance spectroscopy (EIS) is generally used. The EIS measures the impedance response that results from passing an alternating current (AC) signal with a small amplitude across half-cell of three electrode setup at various frequencies ranges from millihertz to megahertz (Panjiara and Pramanik 2021). The EIS also provides the information about electrical properties of the interfaces between the electrocatalyst coated electrode and the electrolyte (Ruiz-Camacho et al., 2017). A widely used approach for graphically representing EIS data is the Nyquist plot. In the Nyquist plot the y-axis represent the imaginary part and x-axis represent the real part. The Nyquist plot used to find the equivalent electrical circuit in order to analyze the electronic properties of the testing electrocatalyst. The Z-view software is used to obtain the quantitative information from the EC (Singh and Pramanik 2022). In general the shape of curves in Nyquist plot is semi-circle a curved or line. Ruiz-Camacho et al., (2017) studied the kinetics and mechanism of ORR on Pt supported on two different type of support (TiO_2-C and SnO_2-C) and the electrochemical properties was compared with the commercial Pt/C (Eteck). It was found from the EIS analysis that TiO_2 and SnO_2 load improve the reaction kinetic to reduce O_2 in acidic medium as shown in Figure 2.6. The arc radius for Pt/C is less than the other two, it means charge transfer resistance is lower for Pt/C.



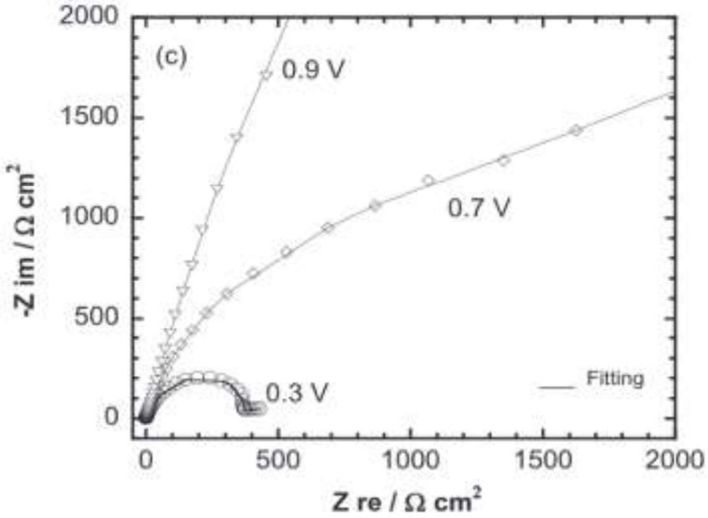


Figure 2.6 Nyquist plot of the ORR on (a) Pt/TiO_2-C, (b) Pt/SnO_2-C and Pt/C (Eteck) in O_2 saturated solution in acidic solution (Ruiz-Camacho et al., 2017).

2.1.1.7 Cathode oxidant

In open literature, many types of oxidant are available for the fuel cell application like pure oxygen, oxygen from air, $KMnO_4$, H_2O_2, NaOCl etc. Sun et al., (2014) uses the air as an oxidant for the PEMFC, although air is cheap, only 21 mol % O_2 is present in air and thus, cell voltage may be low due to low partial pressure as per Nernst equation. The $KMnO_4$ is powerful oxidant but expensive to the other oxidant (Liu et al., 2019). Rathoure and Pramanik (2016) used H_2O_2 solution as an oxidant in microfluidic fuel cell (MFC). However, H_2O_2 decomposes with time, particularly when exposed to heat, light, or contaminants. It may also cause the corrosion with the metal so proper cleaning of cell is required when H_2O_2 used as an oxidant. Yadav and Pramanik (2024) used NaOCl as an oxidant for the direct sodium borohydride fuel cell (DSBFC). It may be hazardous to human health when it is exposed to concentrated NaOCl. On the other side, pure oxygen is preferred due to the high concentration, partial pressure of O_2 at cathode remains always high and thus, high cell voltage is generated to obtain the maximum power density as well as current density

(Singh and Pramanik 2022; Shroti et al 2022; Ohyagi et al., 2013 and Iyuke et al., 2003). Since, air is abundant in the nature and pure oxygen can be easily separate from the air. Moreover, pure O_2 is easily available, cheap, and stable in nature for the fuel cell application. Thus, in the present study pure O_2 was used as oxidant at cathode side.

2.1.1.8 Performance of cathode electrocatalyst

The literature on hydrogen based proton exchange membrane fuel cell indicates that they are still in developing stage for low cost power generation which could be used in wide range of application. In most of the research work, synthesis of cathode electrocatalyst and the performance study in the half-cell and single cell are found in the open literature search (Ramli et al., 2024; Ahn et al., 2021; Mardle et al., 2020 and Lim et al., 2010). Some high performance of PEMFC reported in open literature may be due to different cell operating conditions like very high cell temperature, high metal concentration in the Pt-M/X (where M denotes secondary metal, X denotes support materials e.g., C, MWCNT, NT, C_{BC}, oxNT etc.), different support materials for electrocatalyst, high hydrogen flow rate and different anode/cathode electrocatalyst (Table 2.1). Sun et al, (2022) reported maximum power density of 149.6 mW/cm^2 in a single PEMFC for the cathode electrocatalysts Pt-Co (2:1; 60 wt. %)/MWCNTs. The high performance of the PEMFC may be due to very high temperature of cell i.e., 60 ºC with high concentration of metal i.e., 60 wt. % in Pt-Co(60 wt. %)/MWCNTs having multiwall carbon nanotubes (MWCNTs) as support material which has very high surface area. Shroti et al., (2022) synthesized bimetallic cathode electrocatalyst Pt-Co supported on oxidized multi wall carbon nanotubes as support (oxNT) i.e., Pt-Co (3:1; 30 wt. %)/oxNT. The metal concentration in the Pt-Co catalyst was very high (30 wt. %). The cathode electrocatalyst Pt-Co/oxNT produced OCV of 0.990 V in PEMFC at high metal loading of cathode (1 mg/cm^2) and very high cell operating temperature of 180 ºC. Ohyagi et al.,

(2013) also reported the performance of bi-metallic cathode electrocatalyst Pt-Co(10:1; 51.7 wt. %)/C in a specially designed fuel cell setup for the voltage cycling test under supersaturated humidity condition. The calculated power density was 67.2 mW/cm^2 at a current density of 80.04 mA/cm^2 for the fresh Pt-Co/C cathode. Narayanan and Basu, (2017) reported 43.83mW/cm^2 power density at high hydrogen and oxygen flow rate along with high Pt(40 wt. %)/C cathode electrocatalyst metal loading. Iyuke et al., (2003) reported two types of synthesized cathode electrocatalyst, Pt(10 wt. %)/C$_{AC}$ and Pt(10 wt. %)/C$_{E\text{-}TEK}$ which generate maximum power density of 21.57 mW/cm^2 and 20.32 mW/cm^2, respectively, at high oxygen feeding pressure i.e., 2 atm using high flow channel area of 25 cm^2. According to Polagani et al., (2024) the cathode electrocatalysts Pt-Ni (3:1; 40 wt. %)/C$_{Vulcan\text{-}72R}$ produced a maximum power density of 88 mW/cm^2 in a single PEMFC, at an extremely high hydrogen flow rate of 500 ml/min and oxygen flow rate of 900 ml/min, along with a high metal concentration of 40 wt. % in Pt-Ni(40 wt. %)/C$_{vulcan\text{-}72R}$ cathode electrocatalyst. The surface area of Vulcan-72R carbon support material is very high, it is very costly, and it is also not available easily in the open market commercially. The operating pressure of the PEMFC was high (2 atm). All these factors could be the cause of the high performance of PEMFC reported by Polagani et al., (2024). Thus, it is seen from the thorough literature review on hydrogen based proton exchange membrane fuel cells that the PEMFC performance could be enhanced by the improving the electrocatalytic activity of the cathode electrocatalyst. Also, a detailed study on PEMFC is necessary to improve the performance of fuel cells in terms of maximum power density by optimization of cell variables like anode electrocatalyst type, anode/cathode loading, and cell temperature.

Table 2.1 Performance comparison of different types of electrocatalyst for hydrogen fuel in proton exchange membrane fuel cell.

References	Synthesis method	Process parameters and electrocatalyst used	Cell performance
Sun et al., (2014)	Modified polyol method	Anode: Pt(40 wt. %)/C Loading: 0.4 mg/cm^2 Cathode: Pt-Co(2:1; 60 wt.%)/MWCNTs Loading: 0.4 mg/cm^2 Electrolyte: Nafion® 212 Fuel: hydrogen (100 ml/min); 1 atm Oxidant: air (250 ml/min); 1 atm Cell Temperature: 60 ^{o}C FCA: 5 cm^2 MEA: hot pressed	P_{max}: 149.6 mW/cm^2 OCV: 0.940 V
Ohyagi and Sasaki 2013)	Commercial electrocatalyst	Anode: Pt(47 wt %)/C Loading: 0.4 mg/cm^2 Cathode: Pt-Co (10:1; 51.7 wt. %)/C Loading: 0.4 mg/cm^2 Electrolyte: Nafion® 212 Fuel: hydrogen (100 ml/min), 1 atm; Oxidant: oxygen (400 ml/min), 2 atm; Cell Temperature: 75 ^{o}C FCA: 25 cm^2; MEA: hot pressed	P_{max}: 67.2 mW/cm^2 OCV: 1.0 V
Iyuke et al., (2003)	Commercial electrocatalyst	Anode: Pt(10 wt. %)/C_{AC} Loading: 0.38 mg/cm^2 Cathode: Pt(10 wt. %)/C_{AC} Loading: 0.38 mg/cm^2 Electrolyte: Nafion® 117 Fuel: hydrogen (140 ml), 1 atm Oxidant: oxygen (280 ml), 2 atm Temperature: 25 ^{o}C Flow channel area: 25 cm^2 MEA: hot pressed	P_{max}: 21.57 mW/cm^2 OCV: 1.077 V

References	Synthesis method	Process parameters and electrocatalyst used	Cell performance
Iyuke et al., (2003)	Commercial electrocatalyst	Anode: Pt(10 wt. %)/$C_{E\text{-}TEK}$ Loading: 0.4 mg/cm^2 Cathode: Pt(10 wt. %)/$_{CE\text{-}TEK}$ Loading: 0.4 mg/cm^2 Electrolyte: Nafion® 117 Fuel: hydrogen (140 ml), 1 atm Oxidant: oxygen (280 ml), 2 atm Temperature: 25 °C Flow channel area: 25 cm^2 MEA: hot pressed	P_{max}: 20.32 mW/cm^2 OCV: 0.989 V
Polagani et al., (2024)	Sonochemical method	Anode: Pt(40 wt. %)/C Loading: 0.25 mg/cm^2 Cathode: Pt-Ni(3:1; 40 wt. %)/$C_{vulcan\text{-}72R}$ Loading: 0.4 mg/cm^2 Electrolyte: Nafion® 117 Fuel: hydrogen (500 ml/min); 2 atm Oxidant: oxygen (900 ml/min); 2 atm Cell Temperature: 40 °C FCA: 100 cm^2 MEA: hot pressed	P_{max}: 88 mW/cm^2 OCV: 0.815 V

Abbreviations:

MWCNTs: multiwall carbon nanotubes supported; C_{BC}: black carbon supported; oxNT: oxidized multi wall carbon nanotubes supported; C: carbon supported; C_{AB}: acetylene black; C_{AC}: activated carbon; CNT: carbon nano tube; $C_{Vulcan\text{-}72R}$: Vulcan – 72R carbon; FCA: Flow channel area; MPD: Maximum power density.

2.2 OBJECTIVES

The detailed review of the literature on the synthesis of cathode electrocatalyst revels the necessity of further research and development for hydrogen based proton exchange fuel cells in acidic medium, as positive findings from a single cell investigation in terms of cell voltage and power density was found. The literature review also indicates that the selection of suitable solvent in solvothermal synthesis of electrocatalysts play a key role. The interactions of solvents with reactants, intermediates, and products may have significant effects on reaction equilibriums and reaction kinetics, and products formation. In order to fully understand the many processes that occur in the anode, cathode, and electrolyte of the proton exchange membrane fuel cell, a thorough study is needed. In this context the present thesis has the following objectives:

1. To synthesis carbon supported Pt-based bimetallic electrocatalyst for cathode using different type of solvents.

2. To study the physicochemical properties of the synthesized cathode electrocatalyst.

3. To study the electrochemical properties of synthesized electrocatalyst in half-cell using the three electrode cell assembly.

4. To study the performance of various types of cathode electrocatalyst in a PEMFC to find out the optimum conditions of different parameters like electrocatalyst loading, electrocatalyst types and cell temperature.

5. To optimize the processes parameters by response surface methodology (RSM) and validation by experiments for effective power generation from the PEMFC.

6. To study the stability test of the hydrogen based PEMFC.

The next chapter describes the experimental details associated with the development of proton exchange membrane fuel cell using synthesized cathode electrocatalyst, cathode electrode preparation and characterization using half-cell analysis via cyclic voltammetry followed by electrochemical impedance spectroscopy, single cell performance study, and optimization of process parameters using response surface methodology (RSM) and stability test of a single PEMFC.